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(54) Title: COMPOSITIONS INCLUDING ETHER–CAPPED POLY(OXYALKYLATED) ALCOHOL SURFACTANTS

(57) Abstract

Compositions including ether–capped poly(oxyalkylated) alcohol surfactants having superior grease cleaning abilities and improved spotting/filming benefits are provided . The alcohol surfactants have the formula: $R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$ wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 40, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12; further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof. Various other detergent adjunct ingredients may also be included.

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COMPOSITIONS INCLUDING ETHER-CAPPED POLY(OXYALKYLATED) ALCOHOL SURFACTANTS

Technical Field

The present invention relates to detergent compositions having low-foaming nonionic surfactants and more particularly to compositions for cleaning dishes or hard surfaces having ether-capped poly(oxyalkylated) alcohol surfactants which have superior spotting and filming benefits in dishwashing and hard surface cleaning applications, as well as suds suppression in detergent compositions.

Background of the Invention

Dishwashing and hard surface cleaning, in particular automatic dishwashing in domestic appliances, is an art very different from fabric laundering. Domestic fabric laundering is normally done in purpose-built machines having a tumbling action. These are very different from spray-action domestic automatic dishwashing appliances. The spray action in the latter tends to cause foam. Foam can easily overflow the low sills of domestic dishwashers and slow down the spray action, which in turn reduces the cleaning action. Thus in the distinct field of domestic machine dishwashing, the use of common foam-producing laundry detergent surfactants is normally restricted. These aspects are but a brief illustration of the unique formulation constraints in the domestic dishwashing and hard surface cleaning fields.

One solution to this foaming problem has been to include a suds suppressor, typically a silicone suds suppressor. However, this solution while it works to a certain extent in fabric laundering compositions, fails in domestic dishwashers. The high shear forces involved in domestic dishwashers breaks down the silicone suds suppressors, so any suds suppressors present at the start of the wash is gone before the end. The silicone suds suppressors are not robust enough to survive in the environment of a domestic dishwasher. Even in laundry applications, while less shear than that in a domestic dishwasher, there is still a drop off in suds suppression towards the end of the washing cycle, because of the break down of the silicone suds suppressor. One alternative would be increase the amount of silicone suds suppressor present, however the cost of silicone suds suppressors and the fact that they have a tendency to redeposit on hydrophobic surfaces, such as plastic, makes this an undesirable solution. There remains today the need for a viable and cost

effective alternative to silicone suds suppressor suitable for use in automatic dishwashers as well as laundry washing machines.

On account of the foregoing technical constraints as well as consumer needs and demands, these compositions are undergoing continual change and improvement. Moreover environmental factors such as the restriction of phosphate, the desirability of providing ever-better cleaning results with less product, providing less thermal energy, and less water to assist the washing process, have all driven the need for improved compositions.

However, many compositions heretofore proposed for cleaning dishware and hard surfaces have had aestethic and technical disadvantages, not the least of which is undesirable spots and films on the cleaned surfaces. These undesirable spots and films may be caused by redeposition of soils and cleaning agents such as surfactants which have a low solubility in water. Alternatively, the composition may provide desirable results with respect to undesirable spots and films, and provide excellent cleaning but be totally unsuitable because of the high foam it produces. In addition, there continues to be a need for better cleaning, especially for reduction of spotting and filming and removal of greasy soils. Accordingly, the need remains for compositions which can deliver improved spotting and filming benefits as well as greasy soil removal while providing improved spotting and filming reduction benefits, as well as providing suds suppression which is robust enough to survive the washing environment in which it is deployed.

BACKGROUND ART

U.S. Patent 4,272,394, issued June 9, 1981, U.S. Patent 5,294, 365, issued March 15, 1994 U.S. Patent No. 4,248,729, issued February 3, 1981; U.S. Patent No. 4,284,532, issued August 18, 1981; U.S. Patent No. 4,627,927, issued December 9, 1986; U.S. Patent No. 4,790,856, issued December 13, 1988; U.S. Patent No. 4,804,492, issued February 14, 1989; U.S. Patent No. 4,770,815, issued September 13, 1989; U.S. Patent No. 5,035,814, issued July 30, 1991; U.S. Patent No. 5,047,165, issued September 10, 1991; U.S. Patent No. 5,419,853, issued May 30, 1995; U.S. Patent No 5,294,365, issued March 15, 1994; GB Application No. 2,144,763, published March 13, 1985; GB Application No. 2,154,599, published September 9, 1985; WO Application No. 9,296,150, published April 16, 1992; WO 94/22800, published October 13, 1994, WO 93/04153, published March 4, 1993, WO 97/22651, published June 26, 1997, EP Application No. 342,177, published November 15, 1989 and “Glyceryl Bisether Sulfates. 1: Improved Synthesis” Brian D. Condon; Journal Of the American Chemical Society, Vol. 71, no. 7 (July 1994).

Summary of the Invention

This need is met by the present invention wherein detergent compositions, and in particular, a dish or hard surface cleaning composition having a low-foaming nonionic surfactant are provided. The compositions employ the novel surfactants of the present invention, either alone or in combination with other surfactants, to provide improved spotting and filming performance as well as improved cleaning performance on greasy soils and suds or foam suppression. While not wishing to be bound by theory, it is believed the alcohol surfactants of the present invention deliver superior spotting and filming benefits via improved sheeting action. As for improved cleaning performance on greasy soils, such benefits are shown when the alcohol surfactants of the present invention are employed in conjunction with a high cloud point nonionic surfactant as disclosed in detail herein. Lastly, the alcohol surfactants of the present invention also act to reduce the suds or foaming associated with food soils or various other cleaning agents and allow the use of soluble surfactants, which are high sudsing, such as amine oxides.

In accordance with a first aspect of the present invention, a detergent composition is provided. The composition comprises from about 0.1% to about 15% by weight of the composition of an ether-capped poly(oxyalkylated) alcohol surfactant. The alcohol has the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from about 1 to about 4 carbon atoms; x is an integer having an average value from 1 to about 40, wherein when x is 2 or greater, R^3 may be the same or different and k and j are integers having an average value of from about 1 to about 12, and more preferably 1 to about 5, further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof;

and from about 0.1% to about 99% by weight of the composition of detergent adjunct ingredients.

R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from about 6 to about 22 carbon atoms with about 8 to about 18 carbon atoms being most preferred. R^2 can optionally be alkoxylated, wherein the alkoxy is selected from ethoxy, propoxy,

butyloxy and mixtures thereof. H or a linear aliphatic hydrocarbon radical having from about 1 to about 2 carbon atoms is most preferred for R^3. Preferably, x is an integer having an average value of from about 1 to about 20, more preferably from about 6 to about 15. Also, preferred in the present invention are alcohol surfactants as described above wherein the cloud point of the surfactant is less than about 20°C.

In accordance with a second aspect of the present invention, a method of suds suppression is provided. The method comprises the step of adding an effective amount of a suds suppressing composition to an aqueous cleaning solution, the composition comprising from about 0.1% to about 15% by weight of the composition of an ether-capped poly(oxyalkylated) alcohol surfactant. The alcohol has the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1, R^2, R^3 , x, k and j are hereinbefore defined; and from about 0.1% to about 99% by weight of the composition of detergent adjunct ingredients. Preferably, the aqueous cleaning solution is in a washing appliance, such as a automatic dishwasher. An effective amount of the suds suppressing composition is added to the aqueous cleaning solution, preferably from about 0.1% to about 15% more preferably from about 0.1% to about 10%, even more preferably 0.5% to about 5% by weight

The composition can take granular, tablet or liquid forms including liqui-gels and gels. In addition, the compositions may include adjunct ingredients including builders, surfactants, enzymes, bleaching agents and anti-tarnishing agents.

As already noted, the invention has advantages, including superior spotting and filming reduction benefits as well as excellent greasy soil removal, good dishcare, suds suppression and good overall cleaning.

Accordingly, it is an aspect of the present invention to provide a composition which includes a low-foaming nonionic surfactant having superior spotting and filming reduction benefits as well as excellent greasy soil removal, good dishcare, suds suppression and good overall cleaning. It is a further aspect of the present invention to provide a composition having an ether-capped poly(oxyalkylated) alcohol surfactant. It is a further aspect of the present invention to provide a composition which suppresses or reduces the suds associated with food soils, for example egg soils, or various other cleaning agents, for example surfactants. These and other aspects, features and advantages will be apparent from the following description and the appended claims.

All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig1. is a graph of arm rotation vs. time showing the suds suppressing effect that the novel alcohol surfactants of the present invention has over high sudsing surfactants.

Fig2. is a graph of arm rotation vs. time showing the suds suppressing effect that the novel alcohol surfactants of the present invention has in the presence of high sudsing soil.

Detailed Description of the Preferred Embodiments

Once again, the present invention is directed toward a low-foaming nonionic surfactant for use in detergent compositions. While compositions for cleaning dishes and other hard surfaces are the preferred utility for the surfactants of the present invention, the disclosed compounds may also be employed in laundry and skin care compositions.

The compositions of the present invention comprise the novel alcohol surfactants as disclosed in detail herein and may optionally include various other detergent adjunct ingredients including, but not limited to, detersive enzymes (to assist with tough food cleaning, especially of starchy and proteinaceous soils), builder and a bleaching agent (such as a chlorine bleach or a source of hydrogen peroxide). Bleaching agents useful herein include chlorine oxygen bleaches (e.g., hypochlorite; no NaDCC) and sources of hydrogen peroxide, including any common hydrogen-peroxide releasing salt, such as sodium perborate, sodium percarbonate, and mixtures thereof. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). In the preferred embodiments, additional ingredients such as water-soluble silicates (useful to provide alkalinity and assist in controlling corrosion), dispersant polymers (which modify and inhibit crystal growth of calcium and/or magnesium salts), chelants (which control transition metals), and pH control agents are present. Additional bleach-modifying materials such as conventional bleach activators, e.g. TAED and/or bleach catalysts, may be added, provided that any such bleach-modifying materials are delivered in such a manner as to be compatible with the purposes of the present invention. The present detergent compositions may, moreover, comprise one or more processing aids, fillers, perfumes, conventional enzyme particle-making materials including enzyme cores or "nonpareils", as well as pigments, and the like.

In general, materials used for the production of the compositions herein are preferably checked for compatibility with spotting/filming on surfaces such as glassware. Test methods for spotting/filming are generally described in the automatic dishwashing detergent literature, including DIN and ASTM test methods. Certain oily materials, especially at longer chain lengths, and insoluble materials such as clays, as well as long-chain fatty acids or soaps which form soap scum are therefore preferably limited or excluded from the instant compositions.

Amounts of the essential ingredients can vary within wide ranges, however preferred compositions herein (which typically have a 1% aqueous solution pH of above about 8, more preferably from about 9.5 to about 12, most preferably from about 9.5 to about 11) are those wherein there is present: from about 5% to about 90%, preferably from about 5% to about 75%, of builder; from about 0.1% to about 40%, preferably from about 0.5% to about 30%, of bleaching agent; from about 0.1% to about 15%, preferably from about 0.2% to about 10%, of the nonionic alcohol surfactant; from about 0.0001% to about 1%, preferably from about 0.001% to about 0.05%, of a metal-containing bleach catalyst (most preferred cobalt catalysts useful herein are present at from about 0.001% to about 0.01%); and from about 0.1% to about 40%, preferably from about 0.1% to about 20% of a water-soluble (two ratio) silicate. Such fully-formulated embodiments typically further comprise from about 0.1% to about 15% of a polymeric dispersant, from about 0.01% to about 10% of a chelant, and from about 0.00001% to about 10% of a detersive enzyme, though further additional or adjunct ingredients may be present. Detergent compositions herein in granular or tablet form typically limit water content, for example to less than about 7% free water, for best storage stability. Of course, the compositions may also be in liquid or gel form as well.

While the present invention compositions may be formulated using chlorine-containing bleach additives, preferred compositions of this invention (especially those comprising detersive enzymes) are substantially free of chlorine bleach. By "substantially free" of chlorine bleach is meant that the formulator does not deliberately add a chlorine-containing bleach additive, such as a dichloroisocyanurate, to the preferred composition. However, it is recognized that because of factors outside the control of the formulator, such as chlorination of the water supply, some non-zero amount of chlorine bleach may be present in the wash liquor. The term "substantially free" can be similarly constructed with reference to preferred limitation of other ingredients.

By "effective amount" herein is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance cleaning of a soiled

surface. Likewise, the term "catalytically effective amount" refers to an amount of metal-containing bleach catalyst which is sufficient under whatever comparative test conditions are employed, to enhance cleaning of the soiled surface. In automatic dishwashing, the soiled surface may be, for example, a porcelain cup with tea stain, a porcelain cup with lipstick stain, dishes soiled with simple starches or more complex food soils, or a plastic spatula stained with tomato soup. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some machines have considerably longer wash cycles than others. Some users elect to use warm water without a great deal of heating inside the appliance; others use warm or even cold water fill, followed by a warm-up through a built-in electrical coil. Of course, the performance of bleaches and enzymes will be affected by such considerations, and the levels used in fully-formulated detergent and cleaning compositions can be appropriately adjusted.

Surfactants

The surfactant useful in the present invention compositions is desirably included at levels of from about 0.1% to about 15% of the composition. The surfactant employed in the compositions of the present invention includes a nonionic surfactant or mixtures of various nonionic surfactants. While a wide range of nonionic surfactants may be selected from for purposes of the mixed nonionic surfactants useful in the present invention compositions, it is necessary that the nonionic surfactant at a minimum comprise a surfactant selected from the ether-capped poly(oxyalkylated) alcohols having the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from about 1 to about 4 carbon atoms; x is an integer having an average value from 1 to about 40, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from about 1 to about 12, and more preferably 1 to about 5 further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof.

R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from about 6 to about 22 carbon atoms with about 8 to about 18 carbon atoms being most preferred. Additionally, R^2

may be selected from hydrocarbon radicals which are ethoxylated or propoxylated. H or a linear aliphatic hydrocarbon radical having from about 1 to about 2 carbon atoms is most preferred for R^3. Preferably, x is an integer having an average value of from about 1 to about 20, more preferably from about 6 to about 15.

As described above, when, in the preferred embodiments, and x is greater than 2, R^3 may be the same or different. That is, R^3 may vary between any of the alkyleneoxy units as described above. For instance, if x is 3, R^3may be selected to form ethlyeneoxy(EO) or propyleneoxy(PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and the variation may be much larger with a higher integer value for x and include, for example, multiple (EO) units and a much small number of (PO) units. However, when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl.

Particularly preferred surfactants as described above include those that have a low cloud point of less than about 20°C. These low cloud point surfactants may then be employed in conjunction with a high cloud point surfactant as described in detail below for superior grease cleaning benefits.

Most preferred according to the present invention are those surfactants wherein k is 1 and j is 1 so that the surfactants have the formula:

$$R^1O[CH_2CH(R^3)O]_xCH_2CH(OH)CH_2OR^2$$

where R^1, R^2 and R^3 are defined as above and x is an integer with an average value of from about 1 to about 30, preferably from about 1 to about 20, and even more preferably from about 6 to about 18. Most preferred are surfactants wherein R^1 and R^2 range from about 9 to about 14, R^3 is H forming ethyleneoxy and x ranges from about 6 to about 15.

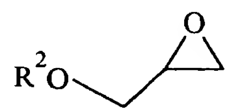
Basically, the alcohol surfactants of the present invention comprise three general components, namely a linear or branched alcohol, an alkylene oxide and an alkyl ether end cap. The alkyl ether end cap and the alcohol serve as a hydrophobic, oil-soluble portion of the molecule while the alkylene oxide group forms the hydrophilic, water-soluble portion of the molecule.

It has been surprisingly discovered in accordance with the present invention that significant improvements in spotting and filming characteristics and, when used inconjunction with high cloud point surfactants, in the removal of greasy soils relative to conventional surfactants, are provided via the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention.

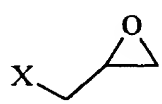
It has been surprisingly discovered that the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention in addition to delivering superior cleaning benefits also provide good suds control. This suds control can be clearly seen in the presence of high sudsing surfactants, such as amine oxides, or in the presence of high sudsing soils, such as protenaeous or egg soils.

Generally speaking, the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention may be produced by reacting an aliphatic alcohol with an epoxide to form an ether which is then reacted with a base to form a second epoxide. The second epoxide is then reacted with an alkoxylated alcohol to form the novel compounds of the present invention.

The process comprises the first step of providing a glycidyl ether having the formula:



where R^2 is defined as above. Various glycidyl ethers are available from a number of commercial sources including the Aldrich Chemical Company. Alternatively, the glycidyl ether may be formed from the reaction of a linear or branched, aliphatic or aromatic alcohol of the formula R^2OH where R^2 is defined as above and an epoxide of the formula:



where X is a suitable leaving group. While a number of leaving groups may be employed in the present invention, X is preferably selected from the group consisting of halides including chloride, bromide, and iodide, tosylate, mesylate and brosylate, with chloride and bromide being even more preferred with chloride being the most preferred (e.g. epichlorohydrin).

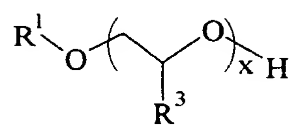
The linear or branched alcohol and the epoxide are preferably reacted at ratios ranging from about 0.5 equivalents alcohol to 2 equivalents epoxide with 0.95 equivalents alcohol to 1.05 equivalents epoxide more typical under acidic conditions for catalysis purposes. Acids which may be employed as catalyst include mineral acids, including but not limited to H_2SO_4 and H_3PO_4 and Lewis acids including, but not limited to, $TiCl_4$, $Ti(O^iPr)_4$, $ZnCl_4$, $SnCl_4$, $AlCl_3$, and BF_3-OEt_2. Preferred catalysts include the Lewis acids with $SnCl_4$ and BF_3-OEt_2 being the most preferred. The catalysts are preferably employed at amounts of about 0.1 mol % to about 2.0 mol % with 0.2 mol % to about 1.0 mol % being more typical.

While the reaction may be conducted in the presence of a suitable solvent such as benzene, toluene, dichloromethane, tetrahydrofuran, diethylether, methyl tert-butylether or the like, the reaction is preferably conducted neat or in the absence of solvent. Lastly, the reaction is conducted at temperatures preferably ranging from about 40°C to about 90°C, more preferably from about 50°C to about 80°C, and most preferably from about 55°C to about 65°C.

Upon completion of the reaction, the mixture is treated with a basic material to form the glycidyl ether. The basic material is preferably a strong base such as a hydroxide. Preferred hydroxides include alkali metal hydroxides with sodium being the typical choice. However, one of ordinary skill in the art will recognize that other basic materials may also be employed. The basic material is preferably added at levels of from about 0.5 equivalents to about 2.5 equivalents, with 0.95 equivalents to 2.0 equivalents being more preferred and 1.0 to 1.5 equivalents being the most preferred.

The product glycidyl ether may then be collected after optional filtration, drying and distillation according to the methods well-known in the art.

To form the surfactant, an ethoxylated alcohol having the formula:



wherein R^1 and x are defined as before in an amount of from about 0.80 to about 1.5 equivalents is combined with a catalyst as described hereinbefore and heated to a temperature ranging from about 50°C to about 95°C and more preferably from about 60°C to about 80°C. The glycidyl ether is then added to the mixture and reacted for from about 0.5 hours to about 30 hours, more preferably from about 1 hour to about 24 hours.

The ether-capped poly(oxyalkylated) alcohol surfactant product is then collect by means common in the art such as filtration. If desired, the surfactant may be further treated by stripping, distillation or various other means before use. The surfactants made the process disclosed herein may contain related impurities which will not adversely affect performance.

A representative synthetic route is demonstrated via the following examples.

EXAMPLE 1

Preparation of $C_{12/13}$-alkyl glycidyl ether

Neodol® 23 (100.00 g, 0.515 mol, available from the Shell Chemical Co.) and tin (IV) chloride (0.58 g, 2.23 mmol, available from Aldrich) are combined in a 500 mL three-necked, round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The mixture is heated to 60 °C. Epichlorohydrin (47.70 g, 0.515 mol, available from Aldrich) is added dropwise so as to keep the temperature between 60-65 °C. After stirring an additional hour at 60 °C, the mixture is cooled to room temperature. The mixture is treated with a 50% solution of sodium hydroxide (61.80 g, 0.773 mol, 50%) while being stirred mechanically. After addition is completed, the mixture is heated to 90 °C for 1.5 h, cooled, and filtered with the aid of ethanol. The filtrate is separated and the organic phase is washed with water (100 mL), dried over $MgSO_4$, filtered, and concentrated. Distillation of the product mixture at 100-120 °C (0.1 mm Hg) providing the glycidyl ether as an oil.

EXAMPLE 2

Preparation of $C_{9/11}$-alkyl glycidyl ether

Neodol® 91 (100.00 g, 0.632 mol available from the Shell Chemical Co.) and tin (IV) chloride (0.82 g, 3.20 mmol available from Aldrich) are combined in a 500 mL three-necked, round-bottomed flask fitted with a condenser, argon inlet, addition funnel, mechanical stirrer and internal temperature probe. The mixture is heated to 65 °C. Epichlorohydrin (58.46 g, 0.632 mol available from Aldrich) is added dropwise so as to keep the temperature between 60-65 °C. After stirring an additional hour at 60 °C, the mixture is cooled to room temperature and is treated with a 50% solution of sodium hydroxide (61.80 g, 0.773 mol, 50%). After addition is completed the mixture is heated to 90 °C for 3.0 h, cooled, and treated with water to dissolve all of the white solids. The organic phase is dried over $MgSO_4$, filtered, and concentrated. Distillation of the product mixture at 100 °C (0.1 mm Hg) provided the gylcidyl ether as an oil.

EXAMPLE 3

Preparation of $C_{12/14}$-alkyl glycidyl ether

The procedure of Example 1 is repeated with the substitution of $C_{12/14}$ fatty alcohol for Neodol® 23.

EXAMPLE 4

Preparation of $C_{14/15}$-alkyl glycidyl ether

The procedure of Example 1 is repeated with the substitution of Neodol® 45 for Neodol® 23.

EXAMPLE 5

Preparation of $C_{14/15}$-alkyl glycidyl ether

The procedure of Example 1 is repeated with the substitution of Tergitol® 15-S-15 for Neodol® 23.

EXAMPLE 6

Preparation of $C_{12/14}$-alkyl-$C_{9/11}$-alkyl ethoxylated ether capped alcohol surfactant

Neodol® 91-8 (16.60 g, 0.0325 mol Shell Chemical Co.) is placed in to a 250ml three necked round bottom flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The contents of the flask are dried under vacuum at 75°C for 15 minutes after establishing an Argon atmosphere, Tin (IV) Chloride (0.25 ml, 2.1 mmol Aldrich) is added to the flask via syringe. The mixture is heated to 60 °C at which point $C_{12/14}$-alkyl glycidyl ether (10.00 g, 0.039 mol) is added dropwise over 15 min while maintaining a temperature of 75-80°C. After stirring for 18 h at 60 °C. The mixture stirs for an additional hour at 75°C until the glycidyl ether is consumed, as determined by TLC. The mixture is cooled to room temperature and diluted with 1 ml of water. The solution is passed through a 170 g of silica gel (Aldrich 227196, 7x12 diameter) while eluting with 5% Methanol (40 ml) dichloromethane. The filtrate is concentrated by rotary evaporation and then stripped in a Kugelrohr oven (70 °C, 0.1 mm Hg for 30 minutes) to yield product as an oil.

EXAMPLE 7

Preparation of $C_{12/14}$-alkyl-$C_{11/15}$-alkyl ethoxylated ether capped alcohol surfactant

Tergitol® 15-S-15 (2820.0 g, 3.275 mol Union Carbide) is melted in to a 12 L three necked round bottom flask fitted with a condenser, argon inlet, addition funnel, mechanical stirrer and internal thermometer. The contents of the flask are dried at 75°C for 30 minutes under vacuum. An argon atmosphere is established. Tin (IV) Chloride (25 ml, 0.214 mmol Aldrich) is added to the flask via syringe. The mixture is heated to 85 °C. $C_{12/14}$-alkyl glycidyl ether (1679.48 g, 6.549 mol) is added dropwise over 1 hour, maintaining the reaction temperature. After stirring for an additional 15 minutes at 75°C, the reaction is quenched with the addition of water (75 ml). The reaction is diluted with 500 ml of 5% methanol dichloromethane. The mixture is cooled to room temperature and then stripped in a Kugelrohr oven (70°C, 0.1 mm Hg for 30 minutes) to yield the surfactant as an oil.

Of course, one of ordinary skill in the art will recognize that the surfactant as described hereinbefore may be employed in combination with other commercially

available nonionic surfactants, particularly low foaming nonionic surfactants (LFNIs) to comprise the surfactant of the present invention.

Low-Foaming Nonionic Surfactant

LFNI may be present in amounts from 0 to about 15% by weight, preferably from about 0.1% to about 10%, and most preferably from about 0.25% to about 4%. LFNIs are most typically used in automatic dishwashing compositions or ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the product. LNFI's also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

Preferred LFNIs include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers. The PO/EO/PO polymer-type surfactants are well-known to have foam suppressing or defoaming action, especially in relation to common food soil ingredients such as egg.

The invention encompasses preferred embodiments wherein LFNI is present, and wherein this component is solid at about 95°F (35°C), more preferably solid at about 77°F (25°C). For ease of manufacture, a preferred LFNI has a melting point between about 77°F (25°C) and about 140°F (60°C), more preferably between about 80°F (26.6°C) and 110°F (43.3°C).

In a preferred embodiment, the LFNI is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis.

A particularly preferred LFNI is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C_{16}-C_{20} alcohol), preferably a C_{18} alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Highly preferred compositions herein wherein the LFNI is present make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from about 20% to about 100%, preferably from about 30% to about 70%, of the total LFNI.

Suitable block polyoxyethylene-polyoxypropylene polymeric compounds that meet the requirements described hereinbefore include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as C_{12-18} aliphatic alcohols, do not generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer surfactant compounds designated PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention.

A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/polyoxypropylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block co-polymer of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

Suitable for use as LFNI in the compositions are those LFNI having relatively low cloud points and high hydrophilic-lipophilic balance (HLB). Cloud points of 1% solutions in water are typically below about 32°C and preferably lower, e.g., 20°C, for optimum control of sudsing throughout a full range of water temperatures.

These and other nonionic surfactants are well known in the art, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detersive Systems", incorporated by reference herein.

Particularly preferred in the present invention are mixed nonionic surfactants. While a wide range of nonionic surfactants may be selected from for purposes of the mixed nonionic surfactant systems useful in the present invention compositions, it is preferred that the nonionic surfactants comprise both a low cloud point surfactant as represented by the ether capped poly(oxyalkylated) alcohol surfactant and high cloud point nonionic surfactant(s) as described as follows. "Cloud point", as used herein, is

a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer, pp. 360-362, hereinbefore).

As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30°C, preferably less than about 20°C, and most preferably less than about 10°C and is represented by the ether-capped poly(oxyalkylated) alcohols as described herein.

Of course, other low-cloud point surfactants may be included in conjunction with the ether-capped poly(oxyalkylated) surfactants. Such optional low-cloud point surfactants include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers. Also, such low cloud point nonionic surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF18) and epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18B series of nonionics, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation). These nonionic surfactants can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred nonionic surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Optional low cloud point nonionic surfactants additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds designated PLURONIC®, REVERSED PLURONIC®, and TETRONIC ® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC ® 25R2 and TETRONIC® 702, Such surfactants are typically useful herein as low cloud point nonionic surfactants.

As used herein, a "high cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of greater than 40°C, preferably greater than about 50°C, and more preferably greater than about 60°C. Preferably the nonionic surfactant system comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, with from about 6 to about 15 moles of ethylene oxide per

mole of alcohol or alkyl phenol on an average basis. Such high cloud point nonionic surfactants include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

It is also preferred for purposes of the present invention that the high cloud point nonionic surfactant further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from about 9 to about 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

Another preferred high cloud point nonionic surfactant is derived from a straight or preferably branched chain or secondary fatty alcohol containing from about 6 to about 20 carbon atoms (C_6-C_{20} alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C9/11 or C11/15 branched alcohol ethoxylates, condensed with an average of from about 6 to about 15 moles, preferably from about 6 to about 12 moles, and most preferably from about 6 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The preferred nonionic surfactant systems useful herein are mixed high cloud point and low cloud point nonionic surfactants combined in a weight ratio preferably within the range of from about 10:1 to about 1:10. Preferred are compositions comprising such mixed nonionic surfactant systems wherein the sudsing (absent any silicone suds controlling agent) is less than 2 inches, preferably less than 1 inch, determined as follows:

Measuring Dishwasher Arm RPM Efficiency and Wash Suds Height:

The equipment useful for these measurements are: a Whirlpool Dishwasher (model 900), or a Miele Dishwasher (model G7750) equipped with clear plexiglass door, IBM computer data collection with Labview and Excel Software, proximity sensor (Newark Corp. - model 95F5203) using SCXI interface, and a plastic ruler.

The data is collected as follows. The proximity sensor is affixed to the bottom dishwasher rack on a metal bracket. The sensor faces downward toward the rotating dishwasher arm on the bottom of the machine (distance approximately 2 cm. from the rotating arm). Each pass of the rotating arm is measured by the proximity sensor and recorded. The pulses recorded by the computer are converted to rotations per minute (RPM) of the bottom arm by counting pulses over a 30 second

interval. The rate of the arm rotation is directly proportional to the amount of suds in the machine and in the dishwasher pump (i.e., the more suds produced, the slower the arm rotation).

The plastic ruler is clipped to the bottom rack of the dishwasher and extends to the floor of the machine. At the end of the wash cycle, the height of the suds is measured using the plastic ruler (viewed through the clear door) and recorded as suds height.

The following procedure is followed for evaluating ADD compositions for suds production as well as for evaluating nonionic surfactants for utility. (For separate evaluation of nonionic surfactant, a base ADD formula, such as Cascade powder, is used along with the nonionic surfactants which are added separately in glass vials to the dishwashing machine.)

First, the machine is filled with water (adjust water for appropriate temperature and hardness) and proceed through a rinse cycle. The RPM is monitored throughout the cycle (approximately 2 min.) without any ADD product (or surfactants) being added (a quality control check to ensure the machine is functioning properly). As the machine begins to fill for the wash cycle, the water is again adjusted for temperature and hardness, and then the ADD product is added to the bottom of the machine (in the case of separately evaluated surfactants, the ADD base formula is first added to the bottom of the machine then the surfactants are added by placing the surfactant-containing glass vials inverted on the top rack of the machine). The RPM is then monitored throughout the wash cycle. At the end of the wash cycle, the suds height is recorded using the plastic ruler. The machine is again filled with water (adjust water for appropriate temperature and hardness) and runs through another rinse cycle. The RPM is monitored throughout this cycle.

An average RPM is calculated for the 1st rinse, main wash, and final rinse. The %RPM efficiency is then calculated by dividing the average RPM for the test surfactants into the average RPM for the control system (base ADD formulation without the nonionic surfactant). The RPM efficiency and suds height measurements are used to dimension the overall suds profile of the surfactant.

To demonstrate the suds control delivered by the nonionic surfactants of the present invention the following experiment is performed. In a Miele G7750, dishwasher, at 7 grains per gallon hardness, nil soil, 48°C fill water temperature and 65°C, wash temperature, the arm rotation was measured over the main wash cycle (from time =0 min to time =27 min) and both rinses (rinse 1 from time = 28 min to time = 33 min, and rinse 2 from time = 34 min to end), for the following compositions:

A. Base granule + 0.5% by weight of an amine oxide of the formula:

$$CH_3(CH_2)_{15}\overset{\overset{\displaystyle O}{|}}{N}(CH_3)_2$$

B. Base granule + 0.5% by weight of an amine oxide used in A and 2% of the nonionic surfactant of example 7.

Arm rotation (in rpm) at time (in minutes):							
Compositions	5	10	15	20	25	30	35
A	48	22	23	24	26	31	40
B	48	47	48	48	47	46	47

See figure 1, for a graph of this information as arm rotation vs. time.

To demonstrate the suds control delivered by the nonionic surfactants of the present invention in the presence of soil and to compare them to known low foaming nonionic surfactants, the following experiment is performed. In a Miele G7750, dishwasher, at 0 grains per gallon hardness, 20g egg soil, 48°C fill water temperature and 65°C, wash temperature, the arm rotation was measured over the main wash cycle (from time =0 min to time =27 min) and both rinses (rinse 1 from time = 28 min to time = 33 min, and rinse 2 from time = 34 min to end), for the following compositions:

C. Base granule + 2% by weight of low foaming nonionic surfactant available from BASF under the name PLURAFAC LF404®

D. Base granule + 2% of the nonionic surfactant of example 7

E. Base granule + 0.5% by weight of an amine oxide used in A above and 2% of the nonionic surfactant of example 7.

Arm rotation (in rpm) at time (in minutes):							
Compositions	5	10	15	20	25	30	35
C	39	30	43	44	46	47	45
D	45	45	46	46	47	46	45
E	46	44	45	47	42	47	45

See figure 2, for a graph of this information as arm rotation vs. time.

The base granule in all compositions comprises(by weight): 53.75% STPP, 14% sodium carbonate, 12% 2R sodium silicate, 12.26% sodium perborate, 0.30%

BTA, 0.5% Paraffin Oil (Winog 70), 1.5% Termamyl/Pentaammineacetatocobalt (III) nitrate granule and 1.27% Bleach stable protease.

It can be clearly seen from the above examples that not only do the nonionic surfactants of the present invention suppresses the suds associated with food soils, in this case egg soils, but they also suppress the suds associated with various other cleaning agents, in this case the suds caused by an amine oxide surfactant. Furthermore, as it is shown above, the nonionic surfactants of the present invention provide better suds control than conventional low foaming nonionic surfactants.

Optional surfactants

Of course, optional detersive surfactants may be included inconjunction with the nonionic surfactants of the present invention. Optional surfactants included in the fully-formulated detergent compositions afforded by the present invention comprises at least 0.01%, preferably from about 0.5% to about 50%, by weight of detergent composition depending upon the particular surfactants used and the desired effects. In a highly preferred embodiment, the detersive surfactant comprises from about 0.5% to about 20% by weight of the composition.

The present invention may also include an anionic co-surfactant. However, the automatic dishwashing detergent compositions herein are preferably substantially free from anionic co-surfactants. It has been discovered that certain anionic co-surfactants, particularly fatty carboxylic acids, can cause unsightly films on dishware. When included, the anionic co-surfactant is typically of a type having good solubility in the presence of calcium. Such anionic co-surfactants are further illustrated by sulfobetaines, alkyl(polyethoxy)sulfates (AES), alkyl (polyethoxy)carboxylates, and short chained C_6-C_{10} alkyl sulfates. However, no such restriction need apply when the compositions are other than automatic dishwashing compositions.

The detersive surfactant can be anionic as discussed above or ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used. Nonlimiting examples of surfactants useful herein include the conventional C_{11}-C_{18} alkyl benzene sulfonates and primary, secondary and random alkyl sulfates, the C_{10}-C_{18} alkyl alkoxy sulfates, the C_{10}-C_{18} alkyl polyglycosides and their corresponding sulfated polyglycosides, C_{12}-C_{18} alpha-sulfonated fatty acid esters, C_{12}-C_{18} betaines and sulfobetaines ("sultaines"), C_{10}-C_{18} amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

Detergent Builders

The present invention may include an optional builder in the product composition. The level of detergent salt/builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% detergent builder and more typically from about 10% to about 80%, even more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate salts are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1} \cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na_2SiO_5 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate salts as builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders may also be added to the present invention as a detergent salt. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions. Aluminosilicate builders include those having the empirical formula:

$$M_z(zAlO_2)_y]\cdot xH_2O$$

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-

trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C_5-C_{20} alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C_{12}-C_{18} monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

<u>Bleaching Agents</u>

Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms. An "effective amount" of a source of hydrogen peroxide is any amount capable of measurably improving stain removal (especially of tea stains) from soiled dishware compared to a hydrogen peroxide source-free composition when the soiled dishware is washed by the consumer in a domestic automatic dishwasher in the presence of alkali.

More generally a source of hydrogen peroxide herein is any convenient compound or mixture which under consumer use conditions provides an effective amount of hydrogen peroxide. Levels may vary widely and are usually in the range from about 0.1% to about 70%, more typically from about 0.5% to about 30%, by weight of the compositions herein.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

While not preferred for compositions of the present invention which comprise detersive enzymes, the present invention compositions may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC").

(a) Bleach Activators

Preferably, the peroxygen bleach component in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8%, by weight of the composition. Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoyl-caprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C_{10}-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and

benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred bleach activators are those described in U.S. Patent 5,130,045, Mitchell et al, and 4,412,934, Chung et al, and copending patent applications U. S. Serial Nos. 08/064,624, 08/064,623, 08/064,621, 08/064,562, 08/064,564, 08/082,270 and copending application to M. Burns, A. D. Willey, R. T. Hartshorn, C. K. Ghosh, entitled "Bleaching Compounds Comprising Peroxyacid Activators Used With Enzymes" and having U.S. Serial No. 08/133,691 (P&G Case 4890R), all of which are incorporated herein by reference.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1 to about 1:1, more preferably from about 10:1 to about 3:1.

Quaternary substituted bleach activators may also be included. The present detergent compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in copending U.S. Patent Nos. 5,460,747, 5,584,888 and 5,578,136, incorporated herein by reference.

(b) Organic Peroxides, especially Diacyl Peroxides

These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming. Preferred is dibenzoyl peroxide.

(c) Metal-containing Bleach Catalysts

The present invention compositions and methods utilize metal-containing bleach catalysts that are effective for use in ADD compositions. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrate having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of

theses catalysts include $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(PF_6)_2$ ("MnTACN"), $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(ClO_4)_2$, $Mn^{IV}_4(u-O)_6(1,4,7\text{-triazacyclononane})_4\text{-}(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2\text{-}(ClO_4)_3$, and mixtures thereof. See also European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful in automatic dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Preferred are cobalt catalysts which have the formula:

$$[Co(NH_3)_n(M')_m]\ Y_y$$

wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); m+n = 6; and Y is an appropriately selected counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[Co(NH_3)_5Cl]\ Y_y$, and especially $[Co(NH_3)_5Cl]Cl_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:

$$[Co(NH_3)_n(M)_m(B)_b]\ T_y$$

wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 M^{-1} s^{-1} (25°C).

Preferred T are selected from the group consisting of chloride, iodide, I_3^-, formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^-, BF_4^-, $B(Ph)_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, etc. Further, T may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

The M moieties include, but are not limited to, for example, F^-, SO_4^{-2}, NCS^-, SCN^-, $S_2O_3^{-2}$, NH_3, PO_4^{3-}, and carboxylates (which preferably are mono-carboxylates, but more than one carboxylate may be present in the moiety as long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., HPO_4^{2-}, HCO_3^-, $H_2PO_4^-$, $HOC(O)CH_2C(O)O$-, etc.) Preferred M moieties are substituted and unsubstituted C_1-C_{30} carboxylic acids having the formulas:

$$RC(O)O-$$

wherein R is preferably selected from the group consisting of hydrogen and C_1-C_{30} (preferably C_1-C_{18}) unsubstituted and substituted alkyl, C_6-C_{30} (preferably C_6-C_{18}) unsubstituted and substituted aryl, and C_3-C_{30} (preferably C_5-C_{18}) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of $-NR'_3$, $-NR'_4{}^+$, $-C(O)OR'$, $-OR'$, $-C(O)NR'_2$, wherein R' is selected from the group consisting of hydrogen and C_1-C_6 moieties. Such substituted R therefore include the moieties $-(CH_2)_nOH$ and $-(CH_2)_nNR'_4{}^+$, wherein n is an integer from 1 to about 16, preferably from about 2 to about 10, and most preferably from about 2 to about 5.

Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, straight or branched C_4-C_{12} alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.

The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as k_{OH}) for cobalt pentaamine catalysts complexed with oxalate (k_{OH}= 2.5 x 10^{-4} M^{-1} s^{-1} (25°C)), NCS^- (k_{OH}= 5.0 x 10^{-4} M^{-1} s^{-1} (25°C)), formate (k_{OH}= 5.8 x 10^{-4} M^{-1} s^{-1} (25°C)), and acetate (k_{OH}= 9.6 x 10^{-4} M^{-1} s^{-1} (25°C)). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]\ T_y$, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$.

Cobalt catalysts according to the present invention made be produced according to the synthetic routes disclosed in U.S. Patent Nos. 5,559,261, 5,581,005, and 5,597,936, the disclosures of which are herein incorporated by reference.

These catalysts may be coprocessed with adjunct materials so as to reduce the color impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the compositions may be manufactured to contain catalyst "speckles".

As a practical matter, and not by way of limitation, the cleaning compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic dishwashing process, typical automatic dishwashing compositions herein will comprise from about 0.0005% to

about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst by weight of the cleaning compositions.

Detersive Enzymes

The compositions of the present invention may also include the presence of at least one detersive enzyme. "Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a composition. Preferred detersive enzymes are hydrolases such as proteases, amylases and lipases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though more bleach compatible, have a remaining degree of bleach deactivation susceptibility.

In general, as noted, preferred compositions herein comprise one or more detersive enzymes. If only one enzyme is used, it is preferably an amyolytic enzyme when the composition is for automatic dishwashing use. Highly preferred for automatic dishwashing is a mixture of proteolytic enzymes and amyloytic enzymes. More generally, the enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders, etc. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated in the instant detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal or soil removal effect on substrates such as fabrics, dishware and the like. Since enzymes are catalytic materials, such amounts may be very small. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 6%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For automatic dishwashing purposes, it may be desirable to increase the active enzyme content of the commercial preparations, in order to minimize the total amount of non-catalytically active materials delivered and thereby improve spotting/filming results.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S as ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985).

An especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of Bacillus amyloliquefaciens subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

Other preferred protease enzymes include protease enzymes which are a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived by replacement of a plurality of amino acid residues of a precursor carbonyl hydrolase with different amino acids, wherein said plurality of amino acid residues replaced in the precursor enzyme correspond to position +210 in combination with one or more of the following residues: +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218 and +222, where the numbered positions correspond to naturally-occurring subtilisin from Bacillus amyloliquefaciens or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins (such as Bacillus lentus subtilisin). Preferred enzymes according include those having position changes +210, +76, +103, +104, +156, and +166.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011

published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Amylases suitable herein include, for example, α-amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo Industries.

Preferred amylases herein have the commonalty of being derived using site-directed mutagenesis from one or more of the Baccillus amylases, especially the Bacillus alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors.

As noted, "oxidative stability-enhanced" amylases are preferred for use herein despite the fact that the invention makes them "optional but preferred" materials rather than essential. Such amylases are non-limitingly illustrated by the following:

(a) An amylase according to the hereinbefore incorporated WO/94/02597, Novo Nordisk A/S, published Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine (preferably threonine), of the methionine residue located in position 197 of the B.licheniformis alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as B. amyloliquefaciens, B.subtilis, or B.stearothermophilus;

(b) Stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from B.licheniformis NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8,15,197,256,304,366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®;

(c) Particularly preferred herein are amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S and are those referred to by the supplier as QL37+M197T.

Cellulases usable in, but not preferred, for the present invention include both bacterial or fungal cellulases. Typically, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas

of a marine mollusk (Dolabella Auricula Solander). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful.

Suitable lipase enzymes for detergent use include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. The LIPOLASE® enzyme derived from Humicola lanuginosa and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein. Another preferred lipase enzyme is the D96L variant of the native Humicola lanuginosa lipase, as described in WO 92/05249 and Research Disclosure No. 35944, March 10, 1994, both published by Novo. In general, lipolytic enzymes are less preferred than amylases and/or proteases for automatic dishwashing embodiments of the present invention.

Peroxidase enzymes can be used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are typically used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S. The present invention encompasses peroxidase-free automatic dishwashing composition embodiments.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent

Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

pH and Buffering Variation

Many detergent compositions herein will be buffered, i.e., they are relatively resistant to pH drop in the presence of acidic soils. However, other compositions herein may have exceptionally low buffering capacity, or may be substantially unbuffered. Techniques for controlling or varying pH at recommended usage levels more generally include the use of not only buffers, but also additional alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art.

The preferred compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. The pH-adjusting components are selected so that when the composition is dissolved in water at a concentration of 1,000 - 10,000 ppm, the pH remains in the range of above about 8, preferably from about 9.5 to about 11. The preferred nonphosphate pH-adjusting component of the invention is selected from the group consisting of:

(i) sodium carbonate or sesquicarbonate;

(ii) sodium silicate, preferably hydrous sodium silicate having $SiO_2:Na_2O$ ratio of from about 1:1 to about 2:1, and mixtures thereof with limited quantities of sodium metasilicate;

(iii) sodium citrate;

(iv) citric acid;

(v) sodium bicarbonate;

(vi) sodium borate, preferably borax;

(vii) sodium hydroxide; and

(viii) mixtures of (i)-(vii).

Preferred embodiments contain low levels of silicate (i.e. from about 3% to about 10% SiO_2).

The amount of the pH adjusting component in the instant composition is preferably from about 1% to about 50%, by weight of the composition. In a preferred embodiment, the pH-adjusting component is present in the composition in an amount from about 5% to about 40%, preferably from about 10% to about 30%, by weight.

Water-Soluble Silicates

The present compositions may further comprise water-soluble silicates. Water-soluble silicates herein are any silicates which are soluble to the extent that they do not adversely affect spotting/filming characteristics of the ADD composition.

Examples of silicates are sodium metasilicate and, more generally, the alkali metal silicates, particularly those having a $SiO_2:Na_2O$ ratio in the range 1.6:1 to 3.2:1; and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6® is a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, Na SKS-6 and other water-soluble silicates useful herein do not contain aluminum. NaSKS-6 is the δ-Na_2SiO_5 form of layered silicate and can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $NaMSi_xO_{2x+1} \cdot yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the α-, β- and γ- forms. Other silicates may also be useful, such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Silicates particularly useful in automatic dishwashing (ADD) applications include granular hydrous 2-ratio silicates such as BRITESIL® H20 from PQ Corp., and the commonly sourced BRITESIL® H24 though liquid grades of various silicates can be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

Chelating Agents

The compositions herein may also optionally contain one or more transition-metal selective sequestrants, "chelants" or "chelating agents", e.g., iron and/or copper and/or manganese chelating agents. Chelating agents suitable for use herein can be selected from the group consisting of aminocarboxylates, phosphonates (especially the aminophosphonates), polyfunctionally-substituted aromatic chelating agents, and mixtures thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to control iron, copper and manganese in washing solutions which are known to decompose hydrogen peroxide and/or bleach activators; other benefits include inorganic film prevention or scale inhibition. Commercial chelating agents for use herein include the DEQUEST® series, and chelants from Monsanto, DuPont, and Nalco, Inc.

Aminocarboxylates useful as optional chelating agents are further illustrated by ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraaminehexacetates, diethylenetriamine-pentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts thereof. In general, chelant mixtures may be used for a combination of functions, such as multiple transition-metal control, long-term product stabilization, and/or control of precipitated transition metal oxides and/or hydroxides.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A highly preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially (but not limited to) the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins. The trisodium salt is preferred though other forms, such as magnesium salts, may also be useful.

Aminophosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are acceptable in detergent compositions, and include the ethylenediaminetetrakis (methylenephosphonates) and the diethylenetriaminepentakis (methylene phosphonates). Preferably, these aminophosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

If utilized, chelating agents or transition-metal-selective sequestrants will preferably comprise from about 0.001% to about 10%, more preferably from about 0.05% to about 1% by weight of the compositions herein.

Dispersant Polymer

Preferred compositions herein may additionally contain a dispersant polymer. When present, a dispersant polymer in the instant compositions is typically at levels in the range from 0 to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 8% by weight of the composition. Dispersant polymers are useful for improved filming performance of the present compositions, especially in higher pH embodiments, such as those in which wash pH exceeds about 9.5. Particularly preferred are polymers which inhibit the deposition of calcium carbonate or magnesium silicate on dishware.

Dispersant polymers suitable for use herein are further illustrated by the film-forming polymers described in U.S. Pat. No. 4,379,080 (Murphy), issued Apr. 5, 1983.

Suitable polymers are preferably at least partially neutralized or alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanolammonium) salts of polycarboxylic acids. The alkali metal, especially sodium salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from about 1,000 to about 500,000, more preferably is from about 1,000 to about 250,000, and most preferably, especially if the composition is for use in North American automatic dishwashing appliances, is from about 1,000 to about 5,000.

Other suitable dispersant polymers include those disclosed in U.S. Patent No. 3,308,067 issued March 7, 1967, to Diehl. Unsaturated monomeric acids that can be polymerized to form suitable dispersant polymers include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence of monomeric segments containing no carboxylate radicals such as methyl vinyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 50% by weight of the dispersant polymer.

Copolymers of acrylamide and acrylate having a molecular weight of from about 3,000 to about 100,000, preferably from about 4,000 to about 20,000, and an acrylamide content of less than about 50%, preferably less than about 20%, by weight of the dispersant polymer can also be used. Most preferably, such dispersant polymer has a molecular weight of from about 4,000 to about 20,000 and an acrylamide content of from about 0% to about 15%, by weight of the polymer.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers. Such copolymers contain as monomer units: a) from about 90% to about 10%, preferably from about 80% to about 20% by weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about 80% by weight of a substituted acrylic monomer or its salt and have the general formula: $-[(C(R^2)C(R^1)(C(O)OR^3)]$ wherein the apparently unfilled valencies are in fact occupied by hydrogen and at least one of the substituents R^1, R^2, or R^3, preferably R^1 or R^2, is a 1 to 4 carbon alkyl or hydroxyalkyl group; R^1 or R^2 can be a hydrogen and R^3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R^1 is methyl, R^2 is hydrogen, and R^3 is sodium.

Suitable low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of about 3,500 and is

the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polyacrylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents 4,530,766, and 5,084,535.

Agglomerated forms of the present compositions may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polyacrylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono- and dicarboxylate monomers are disclosed in European Patent Application No. 66,915, published December 15, 1982.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Michigan. Such compounds for example, having a melting point within the range of from about $30^{o}C$ to about $100^{o}C$, can be obtained at molecular weights of 1,450, 3,400, 4,500, 6,000, 7,400, 9,500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula:
$HO(CH_2CH_2O)_m(CH_2CH(CH_3)O)_n(CH(CH_3)CH_2O)_oOH$ wherein m, n, and o are integers satisfying the molecular weight and temperature requirements given above.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Other suitable dispersant polymers are the carboxylated polysaccharides, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Diehl, issued Mar. 27, 1973; the dextrin esters of polycarboxylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch esters, oxidized starches, dextrins and starch hydrolysates described in U.S. Pat No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches

described in U.S. Pat. No. 3,629,121, Eldib, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDonald, issued Feb. 27, 1979. Preferred cellulose-derived dispersant polymers are the carboxymethyl celluloses.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as polyaspartate.

Material Care Agents

The present compositions may contain one or more material care agents which are effective as corrosion inhibitors and/or anti-tarnish aids. Such materials are preferred components of machine dishwashing compositions especially in certain European countries where the use of electroplated nickel silver and sterling silver is still comparatively common in domestic flatware, or when aluminum protection is a concern and the composition is low in silicate. Generally, such material care agents include metasilicate, silicate, bismuth salts, manganese salts, paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminum fatty acid salts, and mixtures thereof.

When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the ADD composition. Suitable corrosion inhibitors include paraffin oil, typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from about 20 to about 50; preferred paraffin oil is selected from predominantly branched C_{25-45} species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68. A paraffin oil meeting those characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70. Additionally, the addition of low levels of bismuth nitrate (i.e., $Bi(NO_3)_3$) is also preferred.

Other corrosion inhibitor compounds include benzotriazole and comparable compounds; mercaptans or thiols including thionaphtol and thioanthranol; and finely divided Aluminum fatty acid salts, such as aluminum tristearate. The formulator will recognize that such materials will generally be used judiciously and in limited quantities so as to avoid any tendency to produce spots or films on glassware or to compromise the bleaching action of the compositions. For this reason, mercaptan anti-tarnishes which are quite strongly bleach-reactive and common fatty carboxylic acids which precipitate with calcium in particular are preferably avoided.

Silicone and Phosphate Ester Suds Suppressors

The compositions of the invention can optionally contain an alkyl phosphate ester suds suppressor, a silicone suds suppressor, or combinations thereof. Levels in general are from 0% to about 10%, preferably, from about 0.001% to about 5%. However, generally (for cost considerations and/or deposition) preferred compositions herein do not comprise suds suppressors, that is they are totally free of

them, or comprise suds suppressors only at low levels, e.g., less than about 0.1% of active suds suppressing agent.

Silicone suds suppressor technology and other defoaming agents useful herein are extensively documented in "Defoaming, Theory and Industrial Applications", Ed., P.R. Garrett, Marcel Dekker, N.Y., 1973, ISBN 0-8247-8770-6, incorporated herein by reference. See especially the chapters entitled "Foam control in Detergent Products" (Ferch et al) and "Surfactant Antifoams" (Blease et al). See also U.S. Patents 3,933,672 and 4,136,045. Highly preferred silicone suds suppressors are the compounded types known for use in laundry detergents such as heavy-duty granules, although types hitherto used only in heavy-duty liquid detergents may also be incorporated in the instant compositions. For example, polydimethylsiloxanes having trimethylsilyl or alternate endblocking units may be used as the silicone. These may be compounded with silica and/or with surface-active nonsilicon components, as illustrated by a suds suppressor comprising 12% silicone/silica, 18% stearyl alcohol and 70% starch in granular form. A suitable commercial source of the silicone active compounds is Dow Corning Corp.

If it is desired to use a phosphate ester, suitable compounds are disclosed in U.S. Patent 3,314,891, issued April 18, 1967, to Schmolka et al, incorporated herein by reference. Preferred alkyl phosphate esters contain from 16-20 carbon atoms. Highly preferred alkyl phosphate esters are monostearyl acid phosphate or monooleyl acid phosphate, or salts thereof, particularly alkali metal salts, or mixtures thereof.

It has been found preferable to avoid the use of simple calcium-precipitating soaps as antifoams in the present compositions as they tend to deposit on the dishware. Indeed, phosphate esters are not entirely free of such problems and the formulator will generally choose to minimize the content of potentially depositing antifoams in the instant compositions.

Adjunct Materials

Detersive ingredients or adjuncts optionally included in the instant compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. Adjuncts which can also be included in compositions of the present invention, at their conventional art-established levels for use (generally, adjunct materials comprise, in total, from about 30% to about 99.9%, preferably from about 70% to about 95%, by weight of the compositions), include other active ingredients such as non-phosphate builders, chelants, enzymes, dispersant polymers (e.g., from BASF Corp. or Rohm & Haas), color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, silicates, dyes, fillers, germicides, alkalinity sources,

hydrotropes, anti-oxidants, enzyme stabilizing agents, perfumes, solubilizing agents, carriers, processing aids, pigments, and pH control agents.

Depending on whether a greater or lesser degree of compactness is required, filler materials can also be present in the instant compositions. These include sucrose, sucrose esters, sodium sulfate, potassium sulfate, etc., in amounts up to about 70%, preferably from 0% to about 40% of the composition. Preferred filler is sodium sulfate, especially in good grades having at most low levels of trace impurities.

Sodium sulfate used herein preferably has a purity sufficient to ensure it is non-reactive with bleach; it may also be treated with low levels of sequestrants, such as phosphonates or EDDS in magnesium-salt form. Note that preferences, in terms of purity sufficient to avoid decomposing bleach, applies also to pH-adjusting component ingredients, specifically including any silicates used herein.

Hydrotrope materials such as sodium benzene sulfonate, sodium toluene sulfonate, sodium cumene sulfonate, etc., can be present, e.g., for better dispersing surfactant.

Bleach-stable perfumes (stable as to odor); and bleach-stable dyes such as those disclosed in U.S. Patent 4,714,562, Roselle et al, issued December 22, 1987 can also be added to the present compositions in appropriate amounts.

Since the compositions herein can contain water-sensitive ingredients or ingredients which can co-react when brought together in an aqueous environment, it is desirable to keep the free moisture content at a minimum, e.g., 7% or less, preferably 5% or less of the compositions; and to provide packaging which is substantially impermeable to water and carbon dioxide. Coating measures have been described herein to illustrate a way to protect the ingredients from each other and from air and moisture. Plastic bottles, including refillable or recyclable types, as well as conventional barrier cartons or boxes are another helpful means of assuring maximum shelf-storage stability. As noted, when ingredients are not highly compatible, it may further be desirable to coat at least one such ingredient with a low-foaming nonionic surfactant for protection. There are numerous waxy materials which can readily be used to form suitable coated particles of any such otherwise incompatible components; however, the formulator prefers those materials which do not have a marked tendency to deposit or form films on dishes including those of plastic construction.

The following nonlimiting examples further illustrate the present invention.

EXAMPLE 8

An automatic dishwashing detergent composition is prepared as follows:

Ingredients: Weight%

	B	A
Sodium Tripolyphosphate (STPP)	24.0	45
Sodium carbonate	20.0	13.5
Hydrated 2.0r silicate	15	13.5
nonionic surfactants[1]	2.0	2.0
Tergitol 15S9 Nonionic surfactant[2]	1.0	1.0
Polymer[3]	4.0	--
Protease (4% active)	0.83	0.83
Amylase (0.8% active)	0.5	0.5
Perborate monohydrate (15.5% Active AvO)[4]	14.5	14.5
Cobalt catalyst[5]	0.008	--
Water, sodium sulfate and misc.	Balance	Balance

[1] Ether-capped poly(oxyalkylated) alcohol of EXAMPLE 6

[2] Ethoxylated secondary alcohol supplied by Union Carbide (cloud point = 60°C).

[3] Terpolymer selected from either 60% acrylic acid/20% maleic acid/20% ethyl acrylate, or 70% acrylic acid/10% maleic acid/20% ethyl acrylate.

[4] The AvO level of the above formula is 2.2%.

[5] Pentaammineacetatocobalt(III) nitrate.

The ADD's of the above dishwashing detergent composition examples may be used to wash lipstick-stained plastic and ceramic, tea-stained cups, starch-soiled and spaghetti-soiled dishes, milk-soiled glasses, starch, cheese, egg or babyfood-soiled flatware, and tomato-stained plastic spatulas by loading the soiled dishes in a domestic automatic dishwashing appliance and washing using either cold fill, 60°C peak, or uniformly 45-50°C wash cycles with a product concentration of the exemplary compositions of from about 1,000 to about 10,000 ppm, with excellent results.

The following examples further illustrate phosphate built ADD compositions which contain a bleach/enzyme particle, but are not intended to be limiting thereof. All percentages noted are by weight of the finished compositions, other than the perborate (monohydrate) component, which is listed as AvO.

EXAMPLES 9 - 10

	9	10
Catalyst[1]	0.008	0.004
Savinase™ 12T	--	1.1
Protease D	0.9	--

Duramyl™	1.5	0.75
STPP	31.0	30.0
Na_2CO_3	20.0	30.5
Polymer[2]	4.0	--
Perborate (AvO)	2.2	0.7
Dibenzoyl Peroxide	0.2	0.15
2 R Silicate (SiO_2)	8.0	3.5
Paraffin	0.5	0.5
Benzotriazole	0.3	0.15
nonionic surfactant[3]	1.0	1.0

Sodium Sulfate, Moisture ---------Balance----------

[1] Pentaammineacetatocobalt (III) nitrate; may be replaced by MnTACN.

[2] Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers.

[3] A nonionic surfactant prepared according to EXAMPLE 6.

In Compositions of Examples 9 and 10, respectively, the catalyst and enzymes are introduced into the compositions as 200-2400 micron composite particles which are prepared by spray coating, fluidized bed granulation, marumarizing, prilling or flaking/grinding operations. If desired, the protease and amylase enzymes may be separately formed into their respective catalyst/enzyme composite particles, for reasons of stability, and these separate composites added to the compositions.

EXAMPLES 11 and 12

Granular dishwashing detergents are as follows:

	11	12
Composite Particle	1.5	0.75
Savinase™ 12T	2.2	-
Protease D	--	0.45
STPP	34.5	30.0
Na_2CO_3	20.0	30.5
Acusol 480N	4.0	--
Perborate(AvO)	2.2	0.7
2 R Silicate(SiO_2)	8.0	3.5
Paraffin	--	0.5
Benzotriazole	--	0.15
nonionic surfactant[1]	1.0	1.0
LF404[2]	1.0	0.75

Sodium Sulfate, Moisture ---to balance----------

1 Prepared according to EXAMPLE 6.
2 A blend of ehtoxylated/propoxylated nonionic surfactants available from BASF.

EXAMPLE 13

Light-duty liquid dishwashing detergent formulae are prepared as follows:

Composition

Ingredient	A	B	C
		% Weight	
Surfactant[1]	1.00	2.00	1.50
AES	32.00	33.00	29.00
Amine Oxide Surfactant	5.00	4.50	6.00
Betaine Surfactant	3.00	5.00	1.75
Perfume	0.18	0.18	0.18
Water and minors	---------------	Balance	---------------

1 Prepared according to EXAMPLE 6

EXAMPLE 14

An automatic dishwashing detergent tablet is prepared from the composition as follows:

Ingredients:	Weight%	
	A	B
Sodium Tripolyphosphate (STPP)	50.0	47.0
Sodium carbonate	14.0	15
Hydrated 2.0r silicate	8.0	5.0
nonionic surfactant[1]	0.4	2.0
Tergitol 15S9 Nonionic surfactant[2]	1.0	1.0
Polymer[3]	4.0	--
Protease (4% active)	2.0	1.50
Amylase (0.8% active)	---	0.5
Perborate monohydrate (15.5% Active AvO)[4]	1.5	1.5
Cobalt catalyst[5]	0.008	--
TAED	---	2.2
Benzotriazole	0.3	---
Paraffin Oil[6]	0.5	---
Water, sodium sulfate and misc.	Balance	Balance

1 Ether-capped poly(oxyalkylated) alcohol of EXAMPLE 6
2 Ethoxylated secondary alcohol supplied by Union Carbide (cloud point = 60°C).

[3] Polyacrylate polymer blended with HEDP.
[4] The AvO level of the above formula is 2.2%.
[5] Pentaammineacetatocobalt(III) nitrate.
[6] Winog 70 available from Wintershall, Salzbergen, Germany.

The ADD's of the above dishwashing detergent composition examples may be used to wash lipstick-stained plastic and ceramic, tea-stained cups, starch-soiled and spaghetti-soiled dishes, milk-soiled glasses, starch, cheese, egg or babyfood- soiled flatware, and tomato-stained plastic spatulas by loading the soiled dishes in a domestic automatic dishwashing appliance and washing using either cold fill, 60°C peak, or uniformly 45-50°C wash cycles with a product concentration of the exemplary compositions of from about 1,000 to about 10,000 ppm, with excellent results.

EXAMPLE 15

A hard surface cleaning composition of the present invention is illustrated as follows:

Weight %

Ingredients	18	19	20	21	22	23
Surfactant[1]	0.25	3.5	5.5	6.5	6.1	9.5
Sodium hypochlorite	0.9	1.4	1.4	--	--	--
Calcium hypochlorite	--	--	--	0.5	--	--
Sodium dichlorocyanurate	--	--	--	--	1.2	2.0
Tetrapotassium pyrophos.	6.0	--	--	--	13.0	--
Tripotassium phosphate	2.0	--	--	--	12.0	--
Sodium tripolyphosphate	--	--	--	1.6	--	--
Calcium carbonate	--	--	--	--	39.0	1.1
Calcium oxide	--	--	--	--	2.8	--
Perlite abrasive	6.5	--	--	--	22.5	0.5
Sodium hydroxide	0.8	1.6	1.8	0.8	1.1	1.0
Potassium hydroxide	---	--	--	0.85	--	--
Dyes	0.75	0.28	0.28	0.28	--	--
Lanolin	--	--	--	--	--	2.1
Carboxymethylcellulose	--	--	--	--	--	2.6
Water/Misc.	bal.	bal.	bal.	bal.	bal.	bal.

EXAMPLE 16

Liquid gel-like automatic dishwashing detergent compositions according to the present invention as prepared as followed:

STPP builder	17.5	16
K carbonate	8	-
Na carbonate	-	1.5
K hydroxide	2	2.0
K silicate	4	1.5
Na silicate	2	3
thickener	1	1
Nitric acid	0.02	0.02
Al tristearate	0.1	-
polymer dispersant[2]	0.5	-
Na benzoate	0.8	0.5
Surfactant[1]	1.0	2.0
Perborate		2.2
Na hypochlorite	1.5	-
Water and Minors	balance	balance

[1] Ether-capped poly(oxyalkylated) alcohol of EXAMPLE 6
[2] sodium polyacrylate of 4500 m.w.

What is claimed is:

1. A hard surface cleaning composition comprising:

(a) from 0.1% to 15% by weight of the composition of surfactant, wherein said surfactant comprises an ether-capped poly(oxyalylated) alcohol surfactant having the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 40, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12; further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof;

(b) from 0.1% to 99% by weight of the composition of detergent adjunct ingredients.

2. A detergent composition comprising:

(a) from 0.1% to 15% by weight of the composition of surfactant, wherein said surfactant comprises an ether-capped poly(oxyalylated) alcohol surfactant having the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 40, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12; further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof;

(b) from 0.1% to 99% by weight of the composition of detergent adjunct ingredients.

3. An automatic dishwashing composition comprising:

(a) from 0.1% to 15% by weight of the composition of surfactant, wherein said surfactant comprises an ether-capped poly(oxyalylated) alcohol surfactant having the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 40, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12; further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof;

(b) from 0.1% to 99% by weight of the composition of detergent adjunct ingredients.

4. An automatic dishwashing rinse-aid composition comprising:

(a) from 0.1% to 15% by weight of the composition of surfactant, wherein said surfactant comprises an ether-capped poly(oxyalylated) alcohol surfactant having the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 40, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12; further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3

methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof;

(b) from 0.1% to 99% by weight of the composition of detergent adjunct ingredients.

5. The composition according to any of claims 1 to 4 wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic hydrocarbon radicals having from 6 to 22 carbon atoms.

6. The composition according to any of claims 1 to 5 wherein said detergent adjunct ingredients are selected from the group consisting of builders, surfactant, bleaching agents, enzymes, and mixtures thereof.

7. The composition according to any of claims 1 to 6 wherein said composition includes an enzyme selected from the group consisting of protease enzymes, amylase enzymes and mixtures thereof.

8. The composition according to any of claims 1 to 7 wherein said composition includes a bleach system and said bleach system comprises a source of hydrogen peroxide and an additional ingredient selected from bleach activators, bleach catalysts and mixtures thereof.

9. The composition as claimed in Claim 8 wherein said bleach system comprises a source of hydrogen peroxide and a bleach catalyst having the formula:

$$[Co(NH_3)_n(M)_m(B)_b]\ T_y$$

wherein cobalt is in the +3 oxidation state; n is 4 or 5; M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2; B is a ligand coordinated to the cobalt by two sites; b is 0 or 1, and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt; and wherein further said catalyst has a base hydrolysis rate constant of less than 0.23 $M^{-1}\ s^{-1}$ (25°C).

10. The composition according to any of claims 1 to 9 wherein said composition includes an amine oxide.

11. The composition according to any of claims 1 to 10 wherein said composition is free of silicone and phosphate ester suds suppressors.

12. A method of washing tableware in a domestic automatic dishwashing appliance, said method comprising treating the soiled tableware in an automatic dishwasher with an aqueous alkaline bath comprising an automatic dishwashing composition according to any of claims 3 to 10.

13. A method for the suppression of suds, said method comprising the step of adding an effective amount of a suds suppressing composition to an aqueous cleaning solution, said composition comprising:

from about 0.1% to about 15% by weight of the composition of surfactant, wherein said surfactant comprises an ether-capped poly(oxyalylated) alcohol surfactant having the formula:

$$R^1O[CH_2CH(R^3)O]_x[CH_2]_kCH(OH)[CH_2]_jOR^2$$

wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 40, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12; further wherein when x is 15 or greater and R^3 is H and methyl, at least four of R^3 are methyl, further wherein when x is 15 or greater and R^3 includes H and from 1 to 3 methyl groups, then at least one R^3 is ethyl, propyl or butyl, further wherein R^2 can optionally be alkoxylated, wherein said alkoxy is selected from ethoxy, propoxy, butyloxy and mixtures thereof; and

(b) from about 0.1% to about 99% by weight of the composition of detergent adjunct ingredients.

14. A method for the suppression of suds according to claim 13, wherein said aqueous cleaning solution is in an automatic dishwashing appliance.

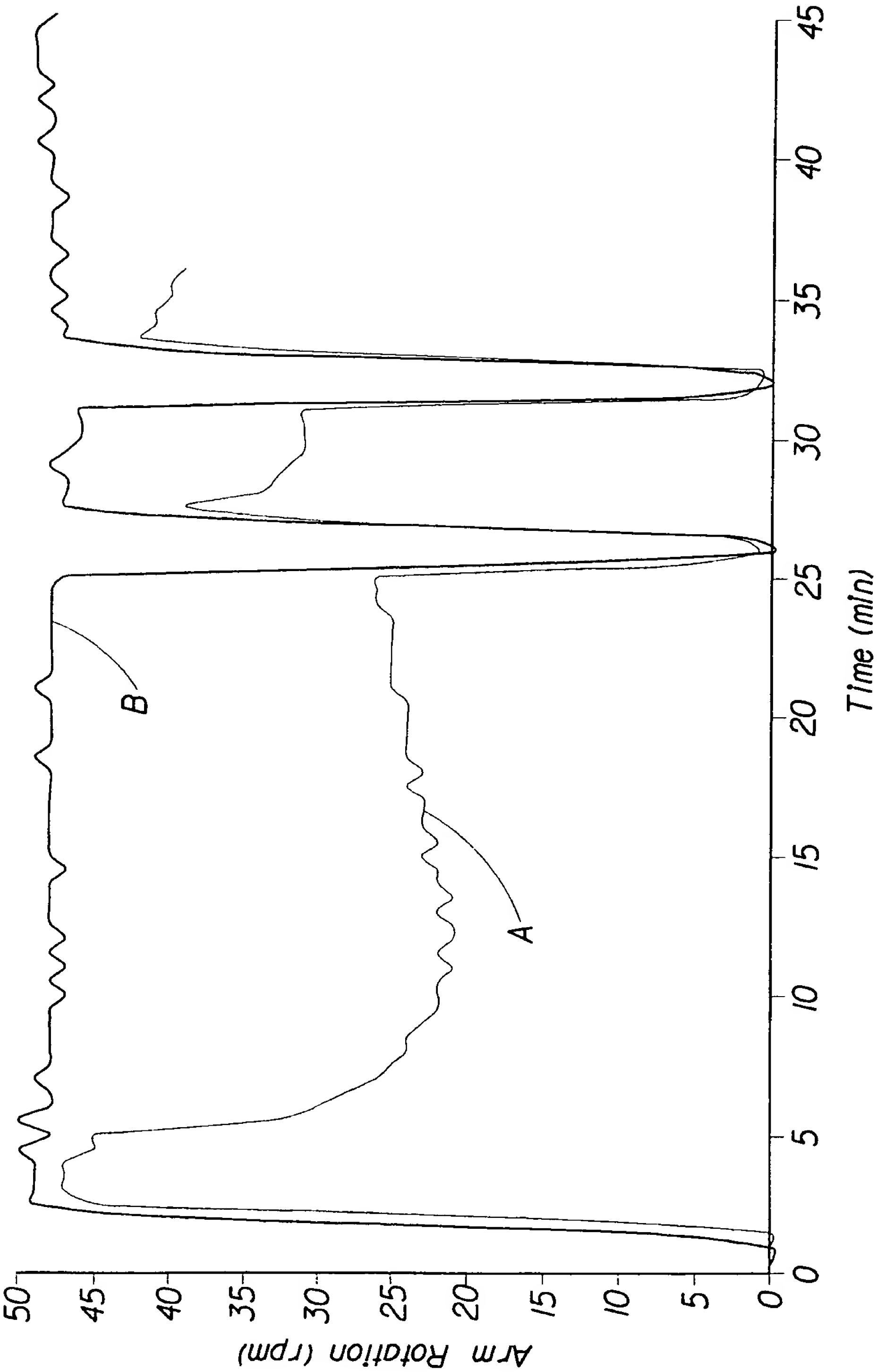


Fig. 1

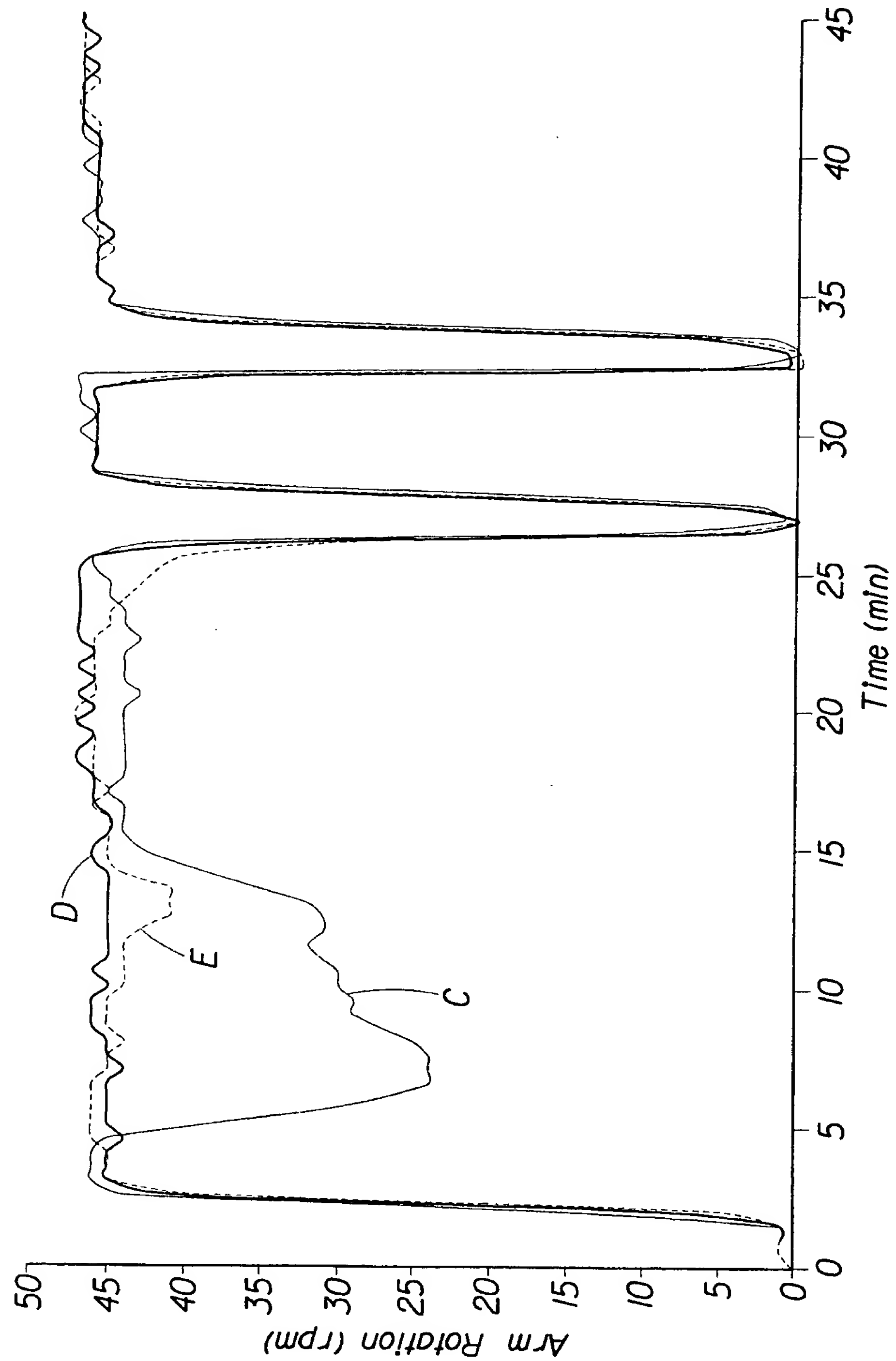


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/15976

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G65/22 C08G65/26 C11D1/72

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 22651 A (PROCTER & GAMBLE) 26 June 1997 cited in the application see examples IX,XI,XII see page 46, line 42 see page 38, paragraph 3 see page 29, line 32 ---	1-4,6-12
X	US 5 294 365 A (BASF CORP.) 15 March 1994 cited in the application see column 4, line 15 - line 17 see examples 1-7; tables 1,3 ---	1-6, 12-14
X	US 4 978 805 A (BAUR RICHARD ET AL) 18 December 1990 see examples 1-7; tables 1,3 see column 4, line 15 - line 17 ---	1-6,11
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 November 1998	04/12/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	O'Sullivan, T

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/15976

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 22 25 318 A (BASF AG) 6 December 1973 see examples 4-6 ---	1
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